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A FIELD TEST FOR LIME-SULPHUR DIPPING BATHS.

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INTRODUCTORY.

The purpose of this paper is to describe a portable testing outfit devised by the writer and employed by the Bureau of Animal Industry for estimating the strength of lime-sulphur dipping baths used in official dipping under regulations now in force.[1] A description of the outfit will be of interest to Federal and State officials concerned with the supervision of dipping, to private parties who wish to control the composition of their dipping baths, and to manufacturers whose dips are subjected to test. This method, however, is intended only for field use; it can not replace in the laboratory the more accurate methods of analysis approved by the Association of Official Agricultural Chemists.

Lime-sulphur dipping baths, whether homemade or proprietary, are essentially composed of two substances in solution, both of which contain sulphur, namely, calcium polysulphid and calcium thiosulphate. The Bureau of Animal Industry has no present proof that calcium thiosulphate is of any value for the treatment of scabies in either cattle or sheep, and pending further investigation, accordingly, must attribute the efficiency of dipping baths solely to the sulphur present in the form of calcium polysulphid.

Many factors may influence the strength of lime-sulphur dipping baths. In the first place, one of the raw materials, lime, is a substance of notoriously uncertain composition as commercially obtainable, and, further, it deteriorates on storage, so that a homemade concentrated dip may turn out much weaker than its maker has cause to suppose. In the second place, solutions of calcium polysulphid are decomposed by contact with air, so that a bath may notably deteriorate even during a single day's dipping. In the

[1] Bureau of Animal Industry Order 210, issued June 18, 1914; reg. 3, sec. 9, p. 19, and reg. 4, sec. 5, p. 23.

Note.—This bulletin describes a portable testing outfit for estimating the strength of lime-sulphur dipping baths; it is of interest to makers and users of such baths, as well as to officials charged with the enforcement of dipping regulations.

absence of a test one faces the alternatives of strengthening slightly used baths by guesswork or of discarding them entirely. A field test is therefore essential to the prosecution of dipping in a manner which shall be at the same time effective and economical.

METHOD OF EXECUTING THE TEST.

The test here described employs the well-known reaction between soluble sulphids and iodin [1] in neutral solution, whereby sulphur is precipitated and a metallic iodid is formed. It therefore directly estimates, not sulphur, but the metal—in this case calcium—combined with sulphur in the form of sulphid or polysulphid. Only in case that sulphur is combined with metal in unvarying proportion can the method also estimate exactly the amount of sulphur present. Theoretically this requirement is not met in the case of lime-sulphur baths, the ratio of lime to sulphur in the mixture of calcium polysulphids which may be present being susceptible to considerable variation. As a matter of fact, however, practical experience of the Bureau of Animal Industry with the test in the field indicates that the ratio in baths prepared after the formulas specified for use in official dipping is near enough to a fixed figure to render the test of entirely adequate accuracy for practical purposes. The ratio provisionally adopted is 4.6 atoms of sulphur to each atom of calcium, or, by weight, 147.5 parts sulphur per 40.07 parts calcium.

Briefly, the method of test involves the addition of standard iodin solution to a measured quantity of bath until the resulting liquid no longer gives color with a dilute alkaline solution of sodium nitroprussid, showing that calcium polysulphid has been entirely decomposed. The amount of iodin added to reach this point is then a measure of the amount of "sulphid sulphur" in the bath. The outfit is pictured in figure 1, and the parts composing it will be described in detail.

PREPARATION OF THE OUTFIT.

I. *The case.*—The carrying case for the outfit is a rectangular box with a hinged cover, made of $\frac{5}{16}$-inch oak, of inside dimensions $7\frac{1}{2}$ by $5\frac{1}{8}$ by $1\frac{7}{8}$ inches. The interior construction, of softer wood, is sufficiently indicated in the diagram. The case must be strongly mortised or nailed together, not simply glued, and should be varnished or painted.[2]

[1] Titration with iodin for determining the "monosulphid equivalent" of lime-sulphur dips seems to have been first seriously proposed by Harris (Michigan Agric. Coll. Exp. Sta. Techn. Bull. No. 6, Jan., 1911). There may be some question regarding the accuracy of the method for exact laboratory analysis, but the uncertainty is not of sufficient seriousness to affect its usefulness for the present purpose.

[2] The cases used by the bureau are painted yellow (yellow being the color of sulphur) to avoid confusion with the similar test case used for arsenical baths (see Department of Agriculture Bulletin 76) which is merely varnished.

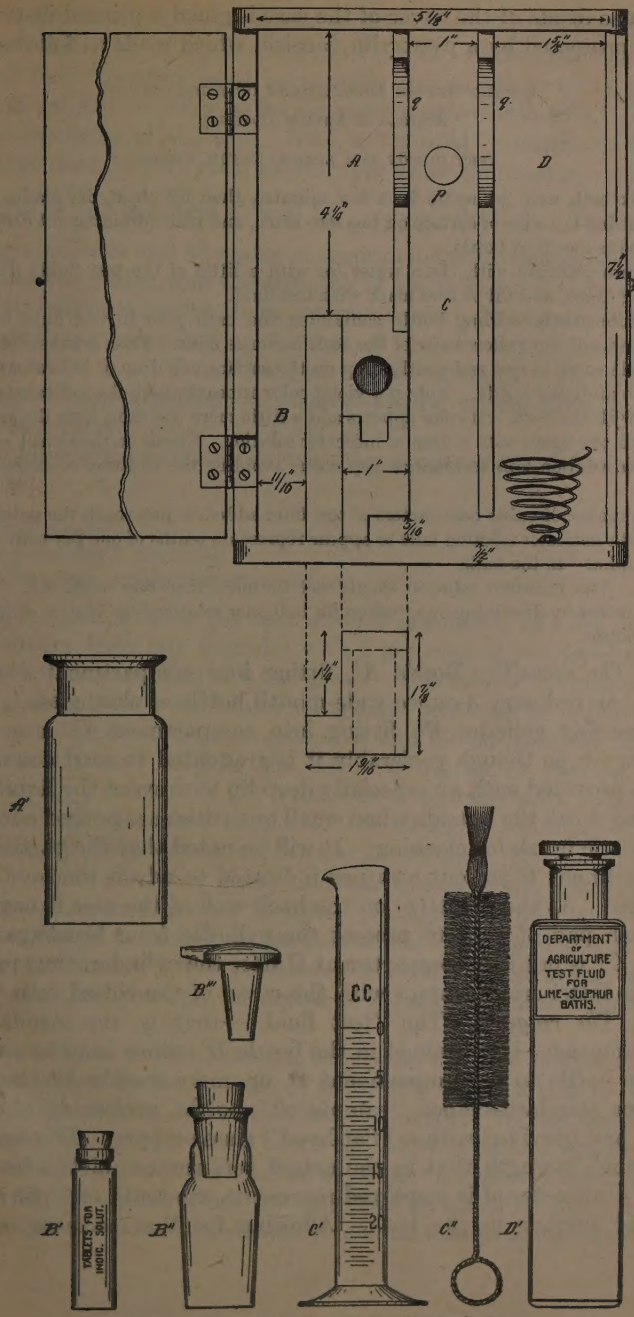

FIG. 1.—Test outfit for lime-sulphur dipping baths.

On the inside of the cover of the case is glued a printed instruction sheet, protected by a pyroxylin varnish, which reads as follows:

UNITED STATES DEPARTMENT OF AGRICULTURE.
Bureau of Animal Industry.

TEST OUTFIT FOR LIME-SULPHUR BATHS.

1. Mix bath well, let settle for a few minutes, then fill clean, dry graduate with bath, setting *top* edge of surface on the zero mark, and pour (draining out drops) into clean, wide-mouthed bottle.

2. Rinse graduate with clean water (or with a little of the test fluid) shake out adhering drops, and fill to zero mark with test fluid.

3. While gently swirling bottle containing the bath pour in test fluid from the graduate until the yellow color of the bath becomes faint. Then let the contents of the bottle come to rest and gently drop on the surface one drop of indicator solution from the dropping bottle. Note if a violet color appears where the indicator solution mixed with the bath. If color appears add a little more test fluid from the graduate, mix, and test again with a drop of indicator solution. Continue thus until a drop of indicator solution fails to produce any color, avoiding the addition of excess of test fluid.

The number of cubic centimeters of test fluid added to just reach the point where color with indicator solution fails to appear represents tenths of one per cent of "sulphid sulphur" in the bath.

Note.—The indicator solution should not be more than one week old. Prepare fresh solution by dissolving one "tablet for indicator solution" in 15 c. c. clean water in the bottle.

II. *The utensils.*—Bottle *A'*, fitting into compartment *A* of the case, is an ordinary 3-ounce wide-mouth bottle of clear glass.

Measuring cylinder *C'*, fitting into compartment *C*, may be of ordinary type though preferably it is graduated to read down only, and is provided with an especially deep lip to prevent the liquid from running down the outside when small quantities are poured out. *C''* is a bristle brush for cleaning. It will be noted that the partitions of compartment *C* are cut away as indicated to admit the foot of the cylinder. At the point (*p*) on the back wall of the case is cemented a $\frac{3}{8}$-inch pad of cork to protect the cylinder from breakage. The brush *C''* is put into compartment *C* after the cylinder, thus protecting the latter from contact with the cover of the closed case.

III. *The reagents.*—The "test fluid,"—that is, the standardized iodin solution—is contained in the bottle *D'*, which may be a special square bottle to fit compartment *D*, or, more readily obtainable, a 4-ounce standard-shaped "sample oil" bottle, preferably of amber glass, and provided with a "flat-hood" glass stopper. The test fluid is of such strength that in the actual performance of the test each cubic centimeter of it employed represents one-tenth of 1 per cent of sulphid sulphur in the bath. Allowing for the meniscus, etc., it

may be assumed nearly enough for practical purposes that the amount of bath delivered by the cylinder is 24 c. c. Each cubic centimeter of test fluid therefore must be actually equivalent to 0.024 gram of sulphid sulphur in order to be apparently equivalent to 0.1 per cent in the execution of the test. Now, a "normal" solution of Ca:4.6S would contain 0.07376 gram sulphur per cubic centimeter; that is, the strength of the test fluid should be $\frac{0.024}{0.07376} = 0.325$ N. In preparing it 44 grams iodin and 88 grams potassium iodid are dissolved in water and made to 1 liter, and the strength of the solution is then adjusted against sodium thiosulphate or arsenious oxid. For example, 50 c. c. of a tenth-normal solution of either of the above standards should require 15.38 c. c. of test fluid of correct strength. The test fluid should, of course, be kept in glass-stoppered bottles only, and in a dark, cool place.

The tablets for indicator solution are prepared after the following formula:

	Grams.
Milk sugar, powdered	12
Sodium nitroprussid, powdered	20
Sodium carbonate, monohydrated, powdered	100

Mix, moisten with 50 per cent alcohol, granulate, and dry at room temperature, then mix granules with 3 per cent of powdered talcum and compress to tablets of 0.255 gram. The tablets are put up in a small glass tube or vial, reinforced against breakage by a glued strip of paper rolled several times around it and folded in at the bottom. After corking and labeling the whole is dipped in paraffin. The tablet vial is put into the left-hand side of compartment *B*, followed by the rubber-stoppered bottle *B''* for indicator solution. This is the standard "TK" dropping bottle, flat stopper, 15 c. c. size, and must be made of amber glass, since the indicator solution is rapidly decomposed upon exposure to light. The glass stopper *B'''* of the dropping bottle is carried in the hole at the right-hand side of compartment *B*, since if left in the bottle for a considerable length of time it may stick fast through the action of the alkaline solution upon the glass.

If the test can not be executed at the vat side the sample of bath should be taken at the vat side in the bottle in which it is to be forwarded. The bottle should be filled to the neck, tightly stoppered, and the stopper and lip of the bottle should be dried and well covered with sealing wax or some similar material, in order to exclude air. Even with these precautions the test must be executed with as little delay as possible, for it has been found that some samples of used

baths decompose upon standing in stoppered bottles, with the result that hydrogen sulphid is formed, and the accuracy of the test is consequently vitiated. The cause and mechanism of this change calls for further study, but there is at present reason to believe that it may be brought about through the action of microorganisms in the bath.

Obviously, if the outfit is used for testing concentrated dips, such should first be diluted with sufficient water to bring the probable content in sulphid sulphur to not much over 2 per cent. Such dilutions may readily be made with the measuring cylinder and wide-mouth bottle provided in the outfit.

UTILIZATION OF RESULTS AFFORDED BY THE TEST.

The object of using such a test as that described is to maintain dipping baths at uniform and effective strength. The test merely indicates the actual strength of the bath, and if the bath is found to be too weak there then remains the task of calculating how much concentrated solution must be added in order to bring it up to the proper strength. Therefore the following tables[1] have been prepared to render the desired information obtainable with a minimum of calculation.

The use of the tables is very simple. For instance, suppose a sheep bath amounting to 1,250 gallons to contain 1.1 per cent sulphid sulphur, as shown by the test, and suppose that a concentrate containing 24 per cent sulphid sulphur (dilution figure 1 to 15) is to be used to strengthen the bath. The table for standardizing sheep baths shows directly that for every 100 gallons of bath in the vat there is needed 1.8 gallons of concentrate, or for the whole, $12.5 \times 1.8 = 22.5$ gallons of concentrate, which quantity is simply to be measured out and added to the bath already in the vat. However, since the bath continually becomes weaker, it is advisable to add somewhat more concentrate than just enough to attain standard strength.

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[1] The formula used to calculate the figures in these tables is $x = 100 \frac{c-a}{b-c}$, in which a=percentage of sulphid sulphur found in the bath by test; b=percentage in the concentrate, and c=standard percentage in bath for dipping.

STANDARDIZING LIME-SULPHUR DIPPING BATHS FOR SHEEP.

Table showing quantity of concentrated dip to be added to each 100 gallons of bath to restore same to standard strength (1.5 per cent sulphid sulphur).

Percentage (on volume) of sulphid sulphur in concentrate.	Dilution figure of concentrate.	Percentage of sulphid sulphur in bath by test—						
		0.8	0.9	1.0	1.1	1.2	1.3	1.4
		Gallons of concentrated dip to be added to 100 gallons of bath.						
Per cent.								
4.5	1 to 2	23.0	20.0	17.0	13.0	10.0	6.7	3.3
4.9	1 to 2½	21.0	18.0	15.0	12.0	8.9	5.9	3.0
5.3	1 to 2½	19.0	16.0	13.0	11.0	8.0	5.3	2.7
5.6	1 to 2⅔	17.0	15.0	12.0	9.7	7.3	4.9	2.4
6.0	1 to 3	16.0	13.0	11.0	8.9	6.7	4.4	2.2
6.4	1 to 3½	14.0	12.0	10.0	8.2	6.2	4.1	2.1
6.8	1 to 3½	13.0	11.0	9.5	7.6	5.7	3.8	1.9
7.5	1 to 4	12.0	10.0	8.3	6.7	5.0	3.3	1.7
8.3	1 to 4½	10.0	8.9	7.4	5.9	4.4	3.0	1.5
9.0	1 to 5	9.3	8.0	6.7	5.3	4.0	2.7	1.3
9.8	1 to 5½	8.5	7.3	6.1	4.9	3.6	2.4	1.2
10.5	1 to 6	7.8	6.7	5.6	4.4	3.3	2.2	1.1
11.2	1 to 6½	7.2	6.2	5.1	4.1	3.1	2.0	1.0
12.0	1 to 7	6.7	5.7	4.8	3.8	2.9	1.9	1.0
13.5	1 to 8	5.8	5.0	4.2	3.3	2.5	1.7	0.8
15.0	1 to 9	5.2	4.4	3.7	3.0	2.2	1.5	0.7
16.5	1 to 10	4.7	4.0	3.3	2.7	2.0	1.3	0.7
18.0	1 to 11	4.2	3.6	3.0	2.4	1.8	1.2	0.6
19.5	1 to 12	3.9	3.3	2.8	2.2	1.7	1.1	0.6
21.0	1 to 13	3.6	3.1	2.6	2.1	1.5	1.0	0.5
22.5	1 to 14	3.3	2.9	2.4	1.9	1.4	1.0	0.5
24.0	1 to 15	3.1	2.7	2.2	1.8	1.3	0.9	0.4
25.5	1 to 16	2.9	2.5	2.1	1.7	1.2	0.8	0.4
27.0	1 to 17	2.7	2.4	2.0	1.6	1.2	0.8	0.4
28.5	1 to 18	2.6	2.2	1.9	1.5	1.1	0.7	0.4
30.0	1 to 19	2.5	2.1	1.8	1.4	1.1	0.7	0.4
31.5	1 to 20	2.3	2.0	1.7	1.3	1.0	0.7	0.3

STANDARDIZING LIME-SULPHUR DIPPING BATHS FOR CATTLE.

Table showing quantity of concentrated dip to be added to each 100 gallons of bath to restore same to standard strength (2 per cent sulphid sulphur).

Per cent (on volume) of sulphid sulphur in concentrate.	Dilution figure of concentrate.	Per cent of sulphid sulphur in bath by test—									
		1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9
		Gallons of concentrated dip to be added to each 100 gallons of bath.									
6.0	1 to 2	25.0	22.0	20.0	17.0	15.0	12.0	10.0	7.5	5.0	2.5
6.5	1 to 2½	22.0	20.0	18.0	16.0	13.0	11.0	8.5	6.7	4.4	2.2
7.0	1 to 2½	20.0	18.0	16.0	14.0	12.0	10.0	8.0	6.0	4.0	2.0
7.5	1 to 2⅔	18.0	16.0	15.0	13.0	11.0	9.1	7.3	5.5	3.6	1.8
8.0	1 to 3	17.0	15.0	13.0	12.0	10.0	8.3	6.7	5.0	3.3	1.7
8.5	1 to 3½	15.0	14.0	12.0	11.0	9.2	7.7	6.2	4.6	3.1	1.5
9.0	1 to 3½	14.0	13.0	11.0	10.0	8.6	7.1	5.7	4.3	2.9	1.4
10.0	1 to 4	13.0	11.0	10.0	8.8	7.5	6.3	5.0	3.8	2.5	1.3
11.0	1 to 4½	11.0	10.0	8.9	7.8	6.7	5.6	4.4	3.3	2.2	1.1
12.0	1 to 5	10.0	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.0
13.0	1 to 5½	9.1	8.2	7.3	6.4	5.5	4.5	3.6	2.7	1.8	0.9
14.0	1 to 6	8.3	7.5	6.7	5.8	5.0	4.2	3.3	2.5	1.7	0.8
15.0	1 to 6½	7.7	6.9	6.1	5.4	4.6	3.8	3.1	2.3	1.5	0.8
16.0	1 to 7	7.1	6.4	5.7	5.0	4.3	3.6	2.9	2.1	1.4	0.7
18.0	1 to 8	6.3	5.6	5.0	4.4	3.7	3.1	2.5	1.9	1.3	0.6
20.0	1 to 9	5.5	5.0	4.4	3.9	3.3	2.8	2.2	1.7	1.1	0.6
22.0	1 to 10	5.0	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5
24.0	1 to 11	4.5	4.1	3.6	3.2	2.7	2.3	1.8	1.4	0.9	0.5
26.0	1 to 12	4.2	3.8	3.3	2.9	2.5	2.1	1.7	1.2	0.8	0.4
28.0	1 to 13	3.8	3.5	3.1	2.7	2.3	1.9	1.5	1.2	0.8	0.4
30.0	1 to 14	3.6	3.2	2.9	2.5	2.1	1.8	1.4	1.1	0.7	0.4
32.0	1 to 15	3.3	3.0	2.7	2.3	2.0	1.7	1.3	1.0	0.7	0.3
34.0	1 to 16	3.1	2.8	2.5	2.2	1.9	1.6	1.2	0.9	0.6	0.3

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